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Original article

Volatilization of [^{14}C]fluoranthene and [^{14}C]diflufenican after soil surface application under field-like conditions: measurement and comparison with different model approaches

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Abstract – The emission of [3-^{14}C]fluoranthene and [pyridine-2-^{14}C]diflufenican after application to bare soil was measured and compared to model predictions. Gaseous losses were determined in a glass wind tunnel under field-like conditions. In several experiments of 13–14 days each, both compounds were sprayed onto the soil surface and the volatilization rates were determined. Measurements showed that the cumulative volatilization of fluoranthene was considerably higher than that of diflufenican. The data obtained were compared with the output of a screening model (BAM) and two estimation methods. Variations in the most sensitive model parameters (e.g. soil moisture and temperature) were investigated by changing the default values used in the model. The influence on the predicted volatilization is discussed in relation to our experimental findings. Several limitations and shortcomings in the current screening and estimation tools for volatilization are characterized and point to the need for an improved physically based model which adequately describes the relevant processes.

BAM / diflufenican / fluoranthene / volatilization / wind tunnel / pesticide / screening model

Résumé – Volatilisation du [^{14}C]fluoranthène et du [^{14}C]difluénican après application à la surface du sol dans des conditions proches de celles au champ : mesures et comparaison avec différents modèles. L'émission du [3-^{14}C]fluoranthène et de [pyridine-2-^{14}C]difluénican après application sur un sol nu a été mesurée et comparée à des prédictions de modèles. Les pertes gazeuses ont été déterminées dans une soufflerie en verre dans des conditions proches de celles au champ. Dans différentes expériences de 13 à 14 jours chacune, les composés ont été pulvérisés sur la surface du sol et le taux de volatilisation cumulée du fluoranthène était considérablement plus grande que celle du difluénican. Les données obtenues ont été comparées avec la sortie d'un modèle de tri (BAM) et deux méthodes d'estimation. Les variations dans les paramètres les plus sensibles du modèle (humidité du sol et température) ont été analysées en changeant les valeurs par défaut du modèle. L'influence sur la volatilisation prédite est discutée en relation avec nos résultats expérimentaux. Plusieurs limitations et insuffisances dans les outils courants de tri et d'estimation pour la volatilisation sont caractérisées et pointent la nécessité d'un modèle amélioré basé sur des lois physiques qui décriraient de façon adéquate les processus pertinents.

BAM / modèle de tri / difluénican / fluoranthène / pesticide / volatilisation / soufflerie

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1. INTRODUCTION

Volatilization from soil and plant surfaces is one of the most important sources of pesticide residues in the atmosphere and thus may lead to contamination by long-range transport and deposition at locations remote from their application [2, 30].

The impacts of these processes have given rise to intensive research concerning the description and characterization of volatilization as documented in numerous review articles [11, 28]. These studies determined the influence of essential factors (e.g. physicochemical parameters of the pesticides, properties of the soil environment) on volatilization rates, but current knowledge is still insufficient to develop a conceptual model for predicting the fate of surface-applied pesticides. Existing approaches and estimations to predict volatilization reflect the crucial soil processes, e.g. transformation, diffusion and convection, with varying degrees of accuracy.

The *Behavior Assessment Model* (BAM) [6–9] was developed for the prediction of the fate of low-concentration pesticides and volatile organics after soil surface application. The BAM calculates the volatilization, degradation and infiltration of these substances under different simplified environmental scenarios [6–9]. The exchange between air and soil is described using the concept of a stagnant boundary layer, based on simplifications concerning the vapor pressure of solubilized chemicals [11]. This basic approach has become part of other screening concepts such as the *Pesticide Leaching and Accumulation Model* (PESTLA) [30, 31].

A second approach to estimating the cumulative volatilization of surface applied pesticides is based on the observed correlation between volatilization data from the literature with the fraction of the pesticide in the gas phase of the topsoil [20]. As a result, a number of easy-to-use regression equations have been derived for greenhouse and field conditions.

Similarly, initial volatilization rates after soil-surface application have been estimated by relating physicochemical properties (e.g. vapor pressure, water solubility) of various pesticides to their published volatilization rates from treated soils [33]. The resulting set of ln-ln correlations has been used to estimate volatilization fluxes.

In addition to these screening tools a great effort has been made to develop 'validated models' (e.g. PESTLA [31]) to calculate *Predicted Environmental Concentrations* (PEC), as a basis for assessing environmental risks. In order to improve the present physically based PEC models, a refinement of the existing process description for volatilization is of the utmost importance for the adequate prediction of the environmental fate of pesticides. At present, pesticide emission by volatilization is poorly represented in the current PEC models. Therefore, it is reasonable to use the current state-of-the-art knowledge on volatilization as a general basis to improve the process descriptions and to include them in PEC groundwater models.

This paper presents data resulting from wind-tunnel experiments and compares them with the output of the screening models and estimation methods mentioned above. The wind-tunnel system containing a lysimeter (*semi-field system*) was developed to approximate field conditions as closely as possible [25, 26]. Furthermore the use of radiolabeled chemicals facilitated the analysis of the test compounds. The studies presented here were carried out with ^{14}C-labeled fluoranthene and ^{14}C-labeled diflufenican. Fluoranthene, (Tab. I) from the group of polycyclic aromatic hydrocarbons (PAHs), was selected as a model chemical because of its ecotoxicological significance, moderate degradability and varying volatilization potential from different surfaces. Diflufenican (Tab. I) is a widely used herbicide which is readily adsorbed by soil [1, 15, 19]. These chemicals were applied to a bare sandy soil (gleyic cambisol) under several scenarios. Volatilization rates were measured [17, 22, 24] and the results obtained were correlated with calculated values.

2. MATERIALS AND METHODS

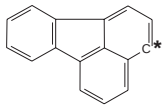
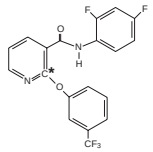
2.1. Test compounds

The PAH fluoranthene (^{14}C-FLA) was obtained from SIGMA-ALDRICH GmbH, Deisenhofen, Germany and diflufenican (^{14}C-DFF) was provided by Rhône-Poulenc Agriculture, Essex, UK. The physicochemical properties of fluoranthene and diflufenican are compiled in Table I.

2.2. Wind-tunnel and air analyses

As an extension of the lysimeter concept [4], a glass wind tunnel was constructed above a 0.5 m^2 lysimeter to measure the gaseous losses of ^{14}C-labeled environmental chemicals under conditions similar to those in the field (Fig. 1). Continuous air sampling to quantify volatile

Table I. Physicochemical data of the test compounds [13, 19].

	Fluoranthene	Diflufenican
Chemical name	Fluoranthene ($C_{16}H_{10}$)	N-(2,4-difluorophenyl)-2-(3-trifluoromethylphenoxy)-nicotinamide ($C_{19}H_{11}F_5N_2O_2$)
Structural formula		
	* = 3-^{14}C-label	* = pyridine-2-^{14}C-label
CAS registry number	206-44-0	83164-33-4
Molecular weight [g·mole^{-1}]	202.26	394.3
Vapor pressure [hPa]	7.0 E-6 @ 20 °C	7.0 E-7 @ 30°C
Water solubility [mg·L^{-1}]	0.21 @ 20 °C	< 0.05 @ 25°C
Henry's law constant K_H	2.7 E-4[a]	3.0 E-6
Organic carbon partition coefficient K_{OC} [cm^3·g^{-1}]	31000-52000	1600-2400

[a] Fendinger & Glotfelty, 1990 [4].

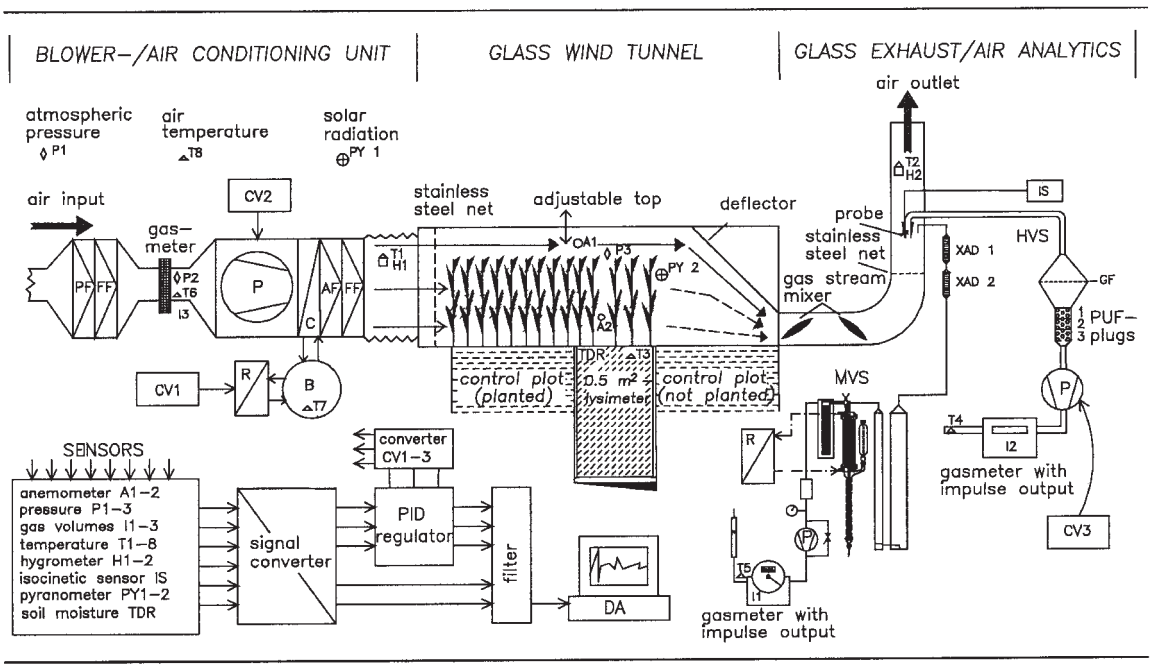


Figure 1. Scheme of the wind tunnel for measuring gaseous losses of pesticides from the soil/plant system under field-like conditions. *AF = active charcoal filter, B = brine tank, C = cooler, CV = converter, DA = data acquisition, FF = fine filter, GF = glass fiber filter, HVS = high-volume sampler (^{14}C organics), MVS = medium-volume sampler ($^{14}CO_2$), P = pump/blower, PF = prefilter, PUF = polyurethane foam, R = refrigeration, TDR = time domain reflectometry, XAD = adsorbing resins (Amberlite XAD-7) [28].*

^{14}C-organic compounds and $^{14}CO_2$ separately, combined with the measurement of the soil/plant residues and leachate, allowed one to obtain complete radioactivity and mass balances of these substances. Automatic measuring and control devices (temperature, moisture content, wind speed) continuously adapted the climate inside the wind tunnel to outside conditions. In addition, a field-like boundary layer profile was obtained inside the wind tunnel, which is of great importance for maintaining realistic soil moisture conditions. Wind speed at a height of 20 cm could be adjusted to 0.3–3.5 m·s^{-1}, corresponding to an air flux of 500–1500 m^3·h^{-1}. ^{14}C-organic compounds in the exhaust air were measured with the high-volume sampler (HVS) consisting of a glass-fiber filter (185 mm o.d.) and three polyurethane foam plugs (PUF) (100 mm o.d. × 150 mm). Aliquots were taken isokinetically based on industrial guidelines for sampling stack air [32]. The maximum sampling rate was 50 m^3·h^{-1} with a minimum and maximum integration period of 1 h and 24 h, respectively. $^{14}CO_2$ was measured with the medium-volume sampler at a sampling rate of 3.5 L·min^{-1} over a maximum integration period of 48 h each. For a detailed description of the system refer to Stork et al. [22, 27, 28].

2.3. Description of the experiments

The herbicide diflufenican and the PAH fluoranthene were applied to the bare soil surface using a semi-automatic application device [22, 23, 27]. In the case of fluoranthene this scenario was intended to simulate an accidental event while diflufenican was applied according to good agricultural practice (Tab. II). Experiments were performed in the wind tunnel under specific climatic conditions adjusted to real outside conditions (Tab. II). Irrigation was applied by a special device.

During the experiments the filter and PUF plugs of the HVS were replaced according to the expected volatilization rates. For the ^{14}C-DFF air samples using the HVS, the filters and PUF plugs were changed at 24 h intervals. For ^{14}C-FLA, the filters and PUF plugs were replaced 1, 3, 6, 12 and 18 h after application. Subsequently they were replaced every 12 h in a diurnal rhythm. PUF plugs were extracted from one to four times with 450 mL toluene (FLA) or acetone (DFF) using a special apparatus [16]. The filters were Soxhlet-extracted for 4 h with either 70 mL toluene (FLA) or 70 mL methanol (DFF). Radioactivity in all samples was measured by liquid scintillation counting (Tri-Carb 2500 TR, Packard). Soil samples were taken at the end of each experiment at depths of 0–2 and 2–7 cm for FLA and 0–5 and 5–10 cm depth for DFF. Total ^{14}C residues in soil were determined by the combustion of aliquots and additionally soil samples (25 g) were Soxhlet-extracted with suitable solvents (FLA: 70 mL acetone, 7 h; DFF: 70 mL methanol, 4 h). Subsequently, non-extractable ^{14}C soil residues were determined. All contaminated parts of the wind tunnel were washed with solvents to yield complete ^{14}C balances. Compound characterization for all fluoranthene samples

Table II. Experimental conditions of the wind-tunnel studies with fluoranthene and diflufenican.

Surface application[a]	**1st fluoranthene experiment**	**2nd fluoranthene experiment**	**diflufenican experiment**
Net applied a.i. [g·ha^{-1}]	112.4	125.3	142.0
^{14}C radioactivity [MBq]	2.06	1.97	13.91
Formulation	SC[b]	SC[b]	SC[b]
Application volume [L·ha^{-1}]	450	450	450
Climatic parameters (mean during experimental periods):			
Air temperature [°C]	16.8	10.1	10.3
Soil temp. (5 cm) [°C]	15.9	10.1	7.2
Air humidity [%$_{rel}$]	81.1	89.1	68.9
Irrigation	1st week none, 2nd week irrigation programme (Σ 17.0 mm)		Σ 77.6 mm
Wind velocity [m·s^{-1}]	0.3/0.9[c]	0.3/1.0[c]	1.5±0,4[d]

[a] Gleyic cambisol: Kaldenkirchen Lower Rhine (pH: 5.35, 0.99% C_{org}, 73.3% sand, 3.6% clay).
[b] Suspendible concentrate based on cyclohexanone.
[c] 1 cm height / 20 cm height.
[d] 20 cm height.

was performed by radio-high performance thin layer chromatography (radio-HPTLC) [17, 24], and for diflufenican by radio-high performance liquid chromatography (radio-HPLC) [22].

2.4. Behavior assessment model (BAM)

The *Behavior Assessment Model* was originally introduced in order to describe transport and loss of soil-applied organic chemicals. It assumes linear, equilibrium partitioning between vapor, liquid and adsorbed chemical phases, net first-order degradation, and chemical movement to the atmosphere by volatilization loss through a stagnant boundary layer at the soil surface [6, 11]. From this description and the assumption of steady-state upward or downward flow, an analytical solution can be derived for the volatilization flux.

This model, which was intended to screen organic compounds for their relative susceptibility to different loss pathways (volatilization, leaching, degradation) in soil and air, requires knowledge of the environmental conditions and physicochemical properties of the compounds. Table III summarizes the parameters used in the calculations.

The BAM was programmed in FORTRAN. The program stores dynamic information for the time period between zero and the user-selected termination time. Values of the chemical volatilization flux are recorded in an output file during the calculation. This file also contains the total concentration of the chemical in the soil as a function of depth. Three scenarios are included during each calculation: steady upward water flux, zero water flux, and steady infiltration flux. At the end of a run a final tabular summary of the mass balance is given.

2.5. Estimation method of Smit et al. (1997)

The estimation method of Smit et al. [20] correlates cumulative volatilization (*CV*) values reported in the literature to the calculated fraction of the pesticide in the gas phase (FP_{gas}).

After spraying, the pesticide is distributed over the gas, liquid, and solid phases of the topsoil layer. Phase partitioning is a well-known method for describing the fractions of the pesticide in the different phases. This method requires values for vapor pressure, water solubility, sorption coefficient and a number of environmental variables as input parameters (Tab. IV). Corrections were made for the effect of temperature on the vapor pressure and water solubility using the Clausius-Clapeyron equation [13].

By correlating the calculated fraction of the pesticide in the gas phase to the cumulative volatilization, regression equations can be derived for various field and greenhouse conditions. The empirical relation for normal to moist field conditions at 21 days after application is:

$$CV = 71.9 + 11.6 \cdot \log [100\, FP_{gas}]$$

where: CV = cumulative volatilization (% of dosage active ingredient)

FP_{gas} = fraction of pesticide in the gas phase.

This equation was the basis for the calculations presented below.

Table III. Default parameter values for the scenarios used in the calculations (BAM).

PARAMETER	FLUORANTHENE	DIFLUFENICAN
Soil porosity	0.468	
Soil bulk density [$g \cdot cm^{-3}$]	1.41	
Organic C fraction	0.0125	
Gaseous diffusion coefficient in air [$cm^2 \cdot d^{-1}$]	4320	
Liquid diffusion coefficient in water [$cm^2 \cdot d^{-1}$]	0.432	
Boundary layer thickness [cm]	0.475	
Depth of incorporation [cm]	0.1	
Henry's law constant K_H	2.7 E-4	3.0 E-6
Organic carbon partition Coefficient K_{OC} [$cm^3 \cdot g^{-1}$]	40000	2000
Degradation half-life [d]	100	210

Table IV. Default parameter values used in the estimation method by Smit et al. [21] and Woodrow et al. [34]. *(Values for soil bulk density, organic carbon partition coefficient and degradation half-life: cf. Tab. II).*

PARAMETER	FLUORANTHENE	DIFLUFENICAN
Molecular weight [g·mole^{-1}]	202.3	394.3
Solubility in water [mg·L^{-1}]	0.21 @ 20 °C	0.05 @ 25 °C
Vapor pressure [mPa]	0.7 @ 20 °C	0.07 @ 30 °C
Organic matter partition coefficient K_{OM} [cm^3·g^{-1}]	22800	1150
Heat of vaporization [kJ·mole^{-1}]	95	
Heat of solution [kJ·mole^{-1}]	27	

2.6. Estimation method of Woodrow et al. (1997)

An approach for estimating volatilization behavior was developed by relating the physicochemical properties of pesticides and other organics to their published volatilization fluxes determined immediately after soil treatment (within 12 ~ 24 h) [33]. The volatilization flux was plotted against the ratio $R_{surf} = [VP / (K_{oc}\, S_w)]$ in a ln-ln-manner for each compound, which resulted in a small scatter about the regression line ln *Flux = 28.355 + 1.6158* ln R_{surf}.

Assuming that the volatilization flux should be directly related to application rate (AR), a further term was added to the above ratio to give $R = [(VP\ AR) / (K_{oc}\, S_w)]$, resulting in the following correlation: ln *Flux = 19.35 + 1.0533* ln *R*. The parameters are given in Table IV.

Both approaches were used in the calculations presented in this article.

3. RESULTS

3.1. Radioactivity balances

The ^{14}C recoveries in the wind-tunnel experiments are summarized in Table V. The functionality of the experimental setup and air sampling unit is illustrated by ^{14}C recoveries of 96.6–101.6% applied radioactivity (AR). System contamination was low (max. 0.4% AR), which can be attributed to the use of glass as the main construction material in combination with high air change rates.

Table V. ^{14}C recoveries of wind-tunnel experiments (*all data in % of net applied radioactivity*).

	1st fluoranthene experiment (Ø air temp. 16.8 °C; Ø soil moist.* 15.8%$_{vol}$)	2nd fluoranthene experiment (Ø air temp. 10.1 °C; Ø soil moist.* 23.1%$_{vol}$)	diflufenican experiment (Ø air temp. 10.3 °C)
Net applied [MBq]	2.06 (= 100%)	1.97 (= 100%)	13.91 (= 100%)
Duration [d]	14	14	13
Contamination**	< 0.1	< 0.1	0.4
Soil	60.0 (0-2 cm)	76.8 (0-2 cm)	96.7 (0-5 cm)
	1.4 (2-7 cm)	4.0 (2-7 cm)	1.1 (5-10 cm)
Leachate	n.d.***	n.d.***	n.d.***
Volatilization	33.6	12.4	0.13
Mineralization	6.6	3.3	0.1
Sum	101.6	96.6	98.4

* Measured at 2 cm depth.
** Contamination of the wind tunnel and the high-volume sampler.
*** n.d. = not detectable.

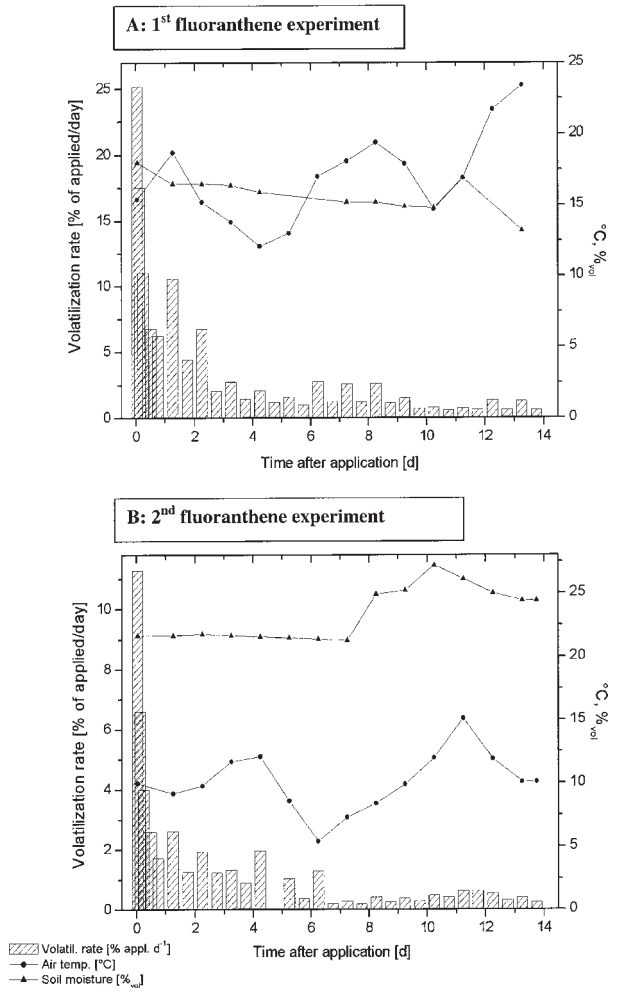


Figure 2. Volatilization rates of [3-^{14}C]fluoranthene after soil surface application. **A**: 1st experiment Ø air temperature 16.8 °C, Ø soil moisture 15.8%$_{vol}$; **B**: 2nd experiment Ø air temperature 10.1 °C, Ø soil moisture 23.1%$_{vol}$.
Climatic parameters are averages within the air sampling periods.

The major fraction of the applied radioactivity was recovered in the soil (61.4–98.8% AR). No radioactivity was detected in the leachate. A moderate mineralization of 3.3–6.6% AR was observed in the fluoranthene experiments whereas the mineralization values within the diflufenican experiments were substantially lower (0.1% AR). More detailed results can be obtained in Stork and Ophoff [17, 22, 24].

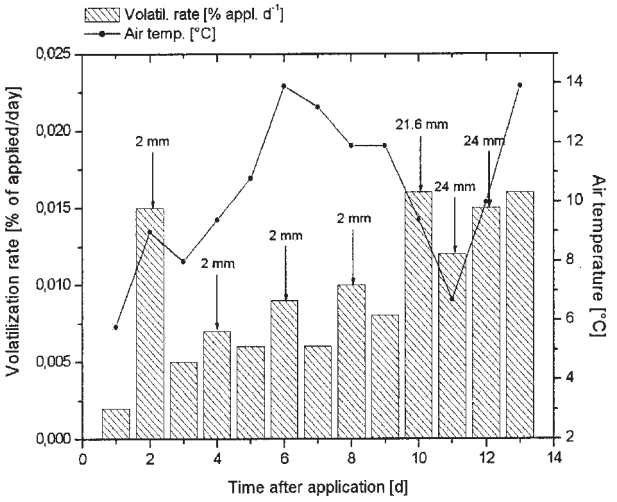


Figure 3. Volatilization rates of [2-pyridine-^{14}C]diflufenican after soil surface application (Ø air temperature 9.7 °C; ↓: irrigation [mm]).
Climatic parameters are averages within the air sampling periods.

3.2. Volatilization

After soil surface application of [3-^{14}C]fluoranthene, 33.6% AR (1st experiment) and 12.4% AR (2nd experiment) were volatilized within the experimental period (14 days). The highest volatilization rates were measured for the first sampling intervals directly after application (Fig. 2). During the following days volatilization rates decreased and finally reached extremely low constant daily rates.

The volatilization showed clear diurnal rhythms, whereby higher temperatures caused increasing volatilization rates of [3-^{14}C]fluoranthene due to increasing vapor pressure. Although a clear dependence of the volatilization rate on the soil moisture was not observed, an indirect influence via soil water evaporation can be assumed.

The results of the diflufenican experiment are shown in Figure 3. The cumulative volatilization within 13 days amounted to 0.13% AR. The volatilization rates ranged between 0.002 and 0.016% AR·d^{-1} and did not decrease during the experimental period. Volatilization rates increased considerably after irrigation. During the experiment soil moisture was not monitored; as a consequence,

increasing soil moisture by irrigation, which may cause a rise in volatilization, can only be assumed. This "irrigation effect" was reduced in the later phases of the experiment. Volatilization of diflufenican was also influenced by the ambient temperature although a diurnal rhythm was not observed due to the 24-hour air collection intervals. The distinct decline in the volatilization rate on the 11th day of the wind-tunnel study in spite of intensive irrigation was accompanied by a simultaneous temperature reduction.

3.3. Screening model (BAM) – Cumulative volatilization

The calculated cumulative volatilization of fluoranthene and diflufenican is summarized in Table VI. Varying parameters are stated explicitly whereas default parameters of the used scenarios are set as mentioned above (Tab. III).

For fluoranthene the model's estimated overall volatilization corresponded well with the measured values. The calculations identified evaporation as the most sensitive parameter influencing volatilization. Increasing the evaporation rates in the simulations related to the 1st experiment (Ø air temp. 16.8 °C; Ø soil moisture 15.8%$_{vol}$) reduced the differences between measured and calculated cumulative volatilization. The simulation of the 2nd experiment, which was performed under moist conditions (Ø air temp. 10.1 °C; Ø soil moisture 23.1%$_{vol}$), resulted in analogous observations. The values calculated for the infiltration rates (19.6% AR) corresponded much better to the measured values (12.4% AR) than those calculated for the evaporation rates (25.1% AR).

Estimations of the parameters for simulating the cumulative volatilization of diflufenican (Tab. VIb) were complicated by the experimental setup of varying irrigation (Fig. 3). The BAM simulations referring to the total experimental period were almost in accordance with the experimental results obtained by using an average value for the evaporation rate (6 mm·d^{-1}) and rather low soil moisture (10%$_{vol}$). On the other hand, the use of average values failed when the behavior of diflufenican after 9 days was simulated. The volatilization determined (0.07% AR) differed markedly from the calculated cumulative volatilization (2.92% AR). This resulted from using an average infiltration rate (1 mm·d^{-1}).

3.4. Simulation model (BAM) – Volatilization rates

The BAM could not satisfactorily predict the measured volatilization rates: immediately after application, measured volatilization of fluoranthene was much higher than predicted by the model (Fig. 4). Due to fixed climate input parameters, the BAM did not reflect the diurnal changes in volatilization, but generally the model

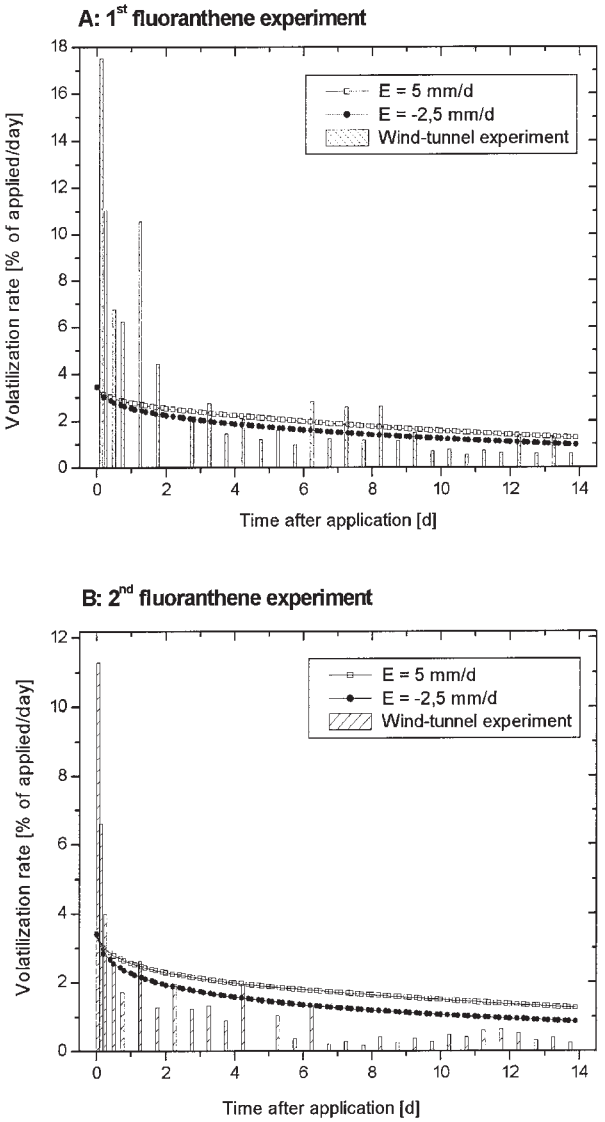


Figure 4. Measured (wind-tunnel experiment) and calculated (BAM) volatilization of fluoranthene after soil surface application. **A**: Ø air temperature 16.8 °C, Ø soil moisture 15.8%$_{vol}$; **B**: Ø air temperature 10.1 °C, Ø soil moisture 23.1%$_{vol}$.
Scenario of simulation: gleyic cambisol, soil moisture 10%$_{vol}$.

Table VI. Comparison of measured (wind-tunnel experiments) and calculated (BAM) cumulative volatilization.
A: Fluoranthene *(data in % of applied radioactivity within 14 days)*; **B**: Diflufenican *(data in % of applied radioactivity)*.

A: Fluoranthene

Scenario	Cumulative volatilization
1st Wind-tunnel experiment (Ø air temp. 16.8 °C; Ø soil moist. 15.8%$_{vol}$)	33.6%
Simulation (BAM) (evaporat. 5 mm·d^{-1})	27.1%
Simulation (BAM) (evaporat. 0 mm·d^{-1})	24.1%
Simulation (BAM) (infiltration 2.5 mm·d^{-1})	22.7%
2nd Wind-tunnel experiment (Ø air temp. 10.1 °C; Ø soil moist. 23.1%$_{vol}$)	12.4%
Simulation (BAM) (evaporat. 5 mm·d^{-1})	25.1%
Simulation (BAM) (evaporat. 0 mm·d^{-1})	21.3%
Simulation (BAM) (infiltration 2.5 mm·d^{-1})	19.6%

B: Diflufenican

Scenario	Cumulative volatilization
Wind-tunnel experiment (Ø air temp. 10.3 °C)	0.13% within 13 days
Simulation (BAM) (evapor. –2.5 mm·d^{-1}; Ø soil moist. 30%$_{vol}$)	3.8% within 13 days
Simulation (BAM) (evapor. –2.5 mm·d^{-1}; Ø soil moist. 10%$_{vol}$)	1.1% within 13 days
Simulation (BAM) (infiltration 6 mm·d^{-1}; Ø soil moist. 30%$_{vol}$)	1.9% within 13 days
Simulation (BAM) (infiltration 6 mm·d^{-1}; Ø soil moist. 20%$_{vol}$)	0.7% within 13 days
Simulation (BAM) (infiltration 6 mm·d^{-1}; Ø soil moist. 10%$_{vol}$)	0.2% within 13 days
Wind-tunnel experiment (Ø air temp. 10.4 °C)	0.07% within 9 days
Simulation (BAM) (infiltration 1 mm·d^{-1}; Ø soil moist. 10%$_{vol}$)	2.92% within 9 days
Simulation (BAM) (infiltration 2.5 mm·d^{-1}; Ø soil moist. 10%$_{vol}$)	1.09% within 9 days

showed a tendency towards enhanced volatilization with increasing temperature for both scenarios.

The daily volatilization rates of diflufenican followed the same two-part kinetics in the course of the simulation. After initially very high volatilization rates, extremely low but constant daily rates were calculated (Fig. 5). This result of the simulation was not verified by the wind-tunnel experiment (Fig. 3), since data was not available for the first hours of the experiment. However, the measured volatilization for the first day indicated that the model significantly overpredicted initial volatilization rates.

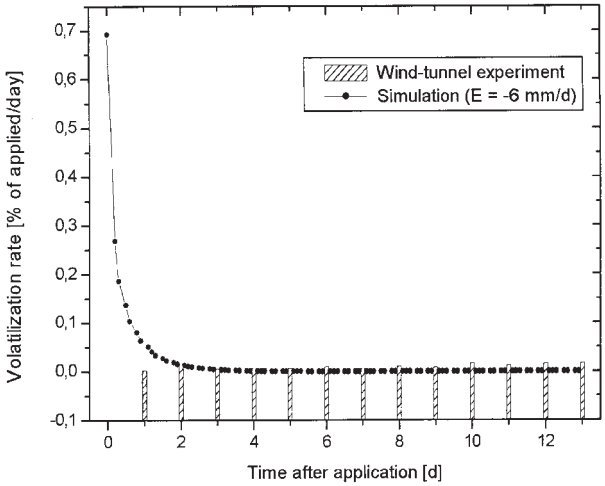


Figure 5. Measured (wind-tunnel experiment) and calculated (BAM) volatilization of diflufenican after soil surface application.
Scenario of simulation: gleyic cambisol, soil moisture 10%$_{vol}$.

3.5. Simulation model (BAM) – Volatilization as a function of soil moisture

In order to characterize the influence of soil moisture on the predicted volatilization rates pure scenario analyses were performed. The range of moisture content within the simulations included the values observed in the experiments.

Figure 6 shows the soil moisture-dependence of volatilization rates without evaporation for fluoranthene and diflufenican after soil surface application.

The model calculated decreasing volatilization rates with increasing soil moisture for both chemicals, except for the volatilization rates for fluoranthene relating to soil moistures of 23% and 35%, which deviated from this observation. The initial period of the simulation of diflufenican showed no specific correlation between volatilization rates and soil moisture, suggesting a more complicated dependence on water content.

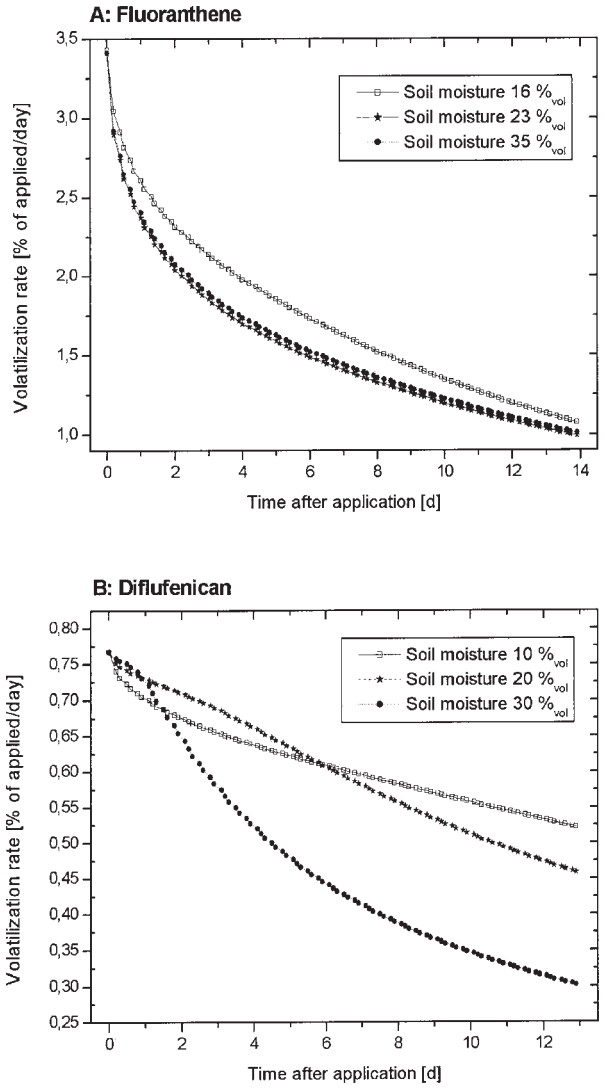


Figure 6. Calculated volatilization (BAM) after soil surface application as a function of soil moisture (**A**: fluoranthene, **B**: diflufenican).
Scenario of simulation: gleyic cambisol, evaporation 0 mm·d^{-1}.

3.6. Estimation method of Smit et al. (1997)

Cumulative volatilization (Tab. VII) was calculated on the basis of the regression equation and the default parameters as mentioned above. Environmental conditions (air temperature, soil moisture) were determined according to the wind-tunnel experiments and were assumed to remain constant during the simulation period (21 days).

The estimated volatilization of fluoranthene (average value 12% at 10.1 °C) is considered to represent realistic values when compared to the measurements (1st experiment: 12.4%). The second scenario (average value 15% at 16.8 °C) also corresponded well with the experimental measurements, within a factor of 2.

The measured volatilization of diflufenican was not in accordance with the computed values. Even distinct variations in the soil moisture could not reduce the differences between measurement and estimation.

In addition, scenario analyses were performed in order to determine the temperature-dependence of the predicted cumulated volatilization using the estimation method. The chosen range of temperature for simulations referring to fluoranthene and diflufenican included the experimental conditions.

The influence of increasing temperatures on the calculated values was characterized by an almost linear increase in the cumulative volatilization (Fig. 7). Remarkably the cumulative volatilization of diflufenican did not fall below 20% AR within the temperature range (5–35 °C).

3.7. Correlation technique for estimating volatilization flux (Woodrow et al., 1997)

Flux values for time periods after application (within 12–24 hours) are calculated by using the correlations and

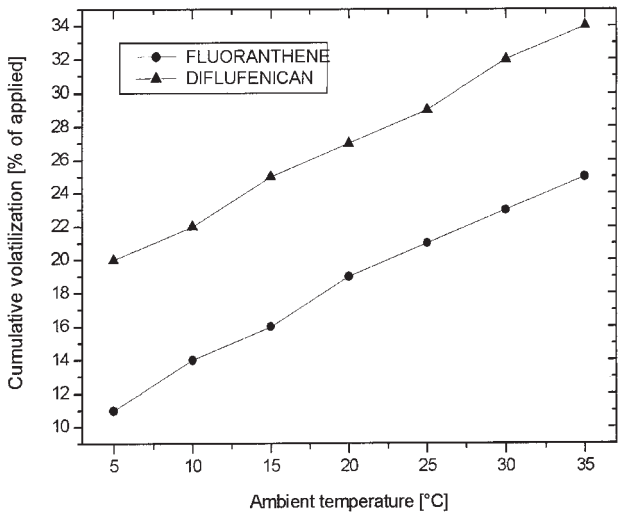


Figure 7. Estimated volatilization of fluoranthene and diflufenican as a function of temperature [21].
Scenario for estimation: gleyic cambisol, soil moisture 10%$_{vol}$.

Table VII. Cumulative volatilization from soil surface estimated by the method of Smit et al. (1997).

COMPOUND	SCENARIO	Field cumulative volatilization (within 21 days)	Measured volatilization
FLUORANTHENE	Ø air temp. 16.8 °C; Ø soil moist. 10.0%$_{vol}$	17%	1st fluoranthene experiment: 33.6% within 14 d
	Ø air temp. 16.8 °C; Ø soil moist. 20.0%$_{vol}$	15%	
	Ø air temp. 16.8 °C; Ø soil moist. 30.0%$_{vol}$	13%	
	Ø air temp. 10.1 °C; Ø soil moist. 10.0%$_{vol}$	14%	2nd fluoranthene experiment: 12.4% within 14 d
	Ø air temp. 10.1 °C; Ø soil moist. 20.0%$_{vol}$	12%	
	Ø air temp. 10.1 °C; Ø soil moist. 30.0%$_{vol}$	10%	
DIFLUFENICAN	Ø air temp. 10.3 °C; Ø soil moist. 10.0%$_{vol}$	22%	Diflufenican experiment: 0.13% within 13 d
	Ø air temp. 10.3 °C; Ø soil moist. 20.0%$_{vol}$	21%	
	Ø air temp. 10.3 °C; Ø soil moist. 30.0%$_{vol}$	18%	

Table VIII. Measured vs. estimated volatilization flux after soil surface application.

COMPOUND	Environmental conditions	Measured volatilization flux [g·ha^{-1}·d^{-1}]	Estimated volatilization flux [g·ha^{-1}·d^{-1}]	
			Correlation with [VP/($K_{oc}S_w$)]	Correlation with [VP×AR/($K_{oc}S_w$)]
FLUORANTHENE	*1st wind-tunnel experiment* Ø air temp. 16.8 °C Ø soil moist. 15.8%$_{vol}$	10.700 (within 18 hours)	1.803	0.213
	2nd wind-tunnel experiment Ø air temp. 10.1 °C Ø soil moist. 23.1%$_{vol}$	4.344 (within 18 hours)		0.238
DIFLUFENICAN	*wind-tunnel experiment* Ø air temp. 10.3 °C	0.003 (within 24 hours)	56.175	2.558

properties as mentioned above (Tab. IV). The use of the ratio [VP/(K_{oc} Sw)] gave results in accordance with the measurements from the wind-tunnel studies, within a factor of 3 (2nd fluoranthene experiment). The estimation for fluoranthene taking into account the application rate resulted in poorer correlations (Tab. VIII). The experimental flux values of diflufenican did not agree with the estimated values.

4. DISCUSSION

Volatilization of fluoranthene exhibits a time-dependent decrease (Fig. 2), as implied by the diffusion-controlled mechanism of category I chemicals [7, 29]. In full accordance with previous findings [5, 29], low volatilization rates led to a steady state with a diurnal rhythm. The low cumulative volatilization of diflufenican (Tab. V) results from its Henry's law constant (Tab. I), corresponding to earlier studies (unpublished data).

In contrast to fluoranthene, diflufenican shows an apparent dependence of volatilization on moisture after application onto bare soil (Fig. 3). Compared to diflufenican, ^{14}C-fluoranthene exhibits an order of magnitude higher adsorption coefficient (Tab. I), so that it is firmly adsorbed on the soil matrix and is no longer desorbable even if the soil is remoistened.

Application of the *Behavior Assessment Model* (BAM) using averaged values (e.g. environmental conditions and pesticide properties) enabled us to calculate the influence of varying parameters on volatilization.

Differences between measured and calculated values became obvious during the initial phases. For example, immediately after application of fluoranthene, measured volatilization was much higher than predicted by the model. This suggests that the model is not able to reflect

the non-equilibrium conditions (higher amounts of fluoranthene available in soil solution) at the initial stage.

Basic assumptions of the model (e.g. linear adsorption isotherm, first-order degradation, steady state) are far too simplified and this limits the representation of field conditions.

The applied input parameters entail other problems. For example, it was not considered in the calculations that the physicochemical properties of the chemicals may change during the experiment due to different soil conditions. The average values (infiltration rate and soil moisture) used for calculating the cumulative volatilization of diflufenican hardly reflect the experimental conditions which were characterized by irrigation in the final period (Fig. 3).

In general, the model calculated decreasing volatilization with increasing soil moisture for both fluoranthene and diflufenican (Fig. 6). However, the opposite is true for pesticides [5, 21]. The authors of the BAM pointed out the differences between measured and calculated values [9, 11] and emphasized that the BAM is not a simulation model so that behavior under field conditions (e.g. increased adsorption during soil drying) is not taken into account. The BAM merely seeks to describe the behavior of one chemical relative to another under a standard prescribed set of conditions and has therefore been developed as a screening model.

The estimation method [20] was used to calculate the cumulative volatilization of diflufenican and fluoranthene during a period of 21 days, applying their concentrations in the gas phase as input variables. The effect of temperature on the physicochemical properties was taken into account. This approach has a number of limitations and shortcomings which have already been discussed [20, 30]. Similar to the BAM the environmental conditions and properties of the chemicals are assumed to remain constant during the period of volatilization. In addition, uncertainty in the calculated cumulative loss depends on the quality of the underlying data used in the respective correlations [30].

A similar correlation between the logarithm of the ratio of the vapor pressure divided by the water solubility and the organic carbon sorption coefficient (K_{oc}) and the logarithm of the volatilization rate as measured during the first day after application, was derived by Woodrow et al. (1997). Some of the data used in the correlation were obtained by residue analysis, which provides an indirect measurement of the total flux.

Due to related assumptions and equations the results of both screening-level estimations are rather similar. In contrast to the simulations of fluoranthene volatilization, which were in good accordance with the experimental results, the calculated volatilization rates for diflufenican agreed poorly with the measured values.

The results of the present investigations confirm the need for a comprehensive model which combines the influence of the physicochemical properties of pesticides with an accurate description of the relevant transfer processes. Improvements reflecting the temperature dependence of parameters, photodegradation [14] and non-equilibrium conditions (e.g. phase distributions) may help to elucidate the mechanisms involved in the volatilization of pesticides. In addition to volatilization from soil surfaces, pesticides located on plant surfaces also make a large contribution to atmospheric contamination. No reliable model is yet available to predict the potential of volatilization of pesticides from soil and plants [30]. As a consequence, detailed investigations varying critical parameters that can lead to a better understanding of key processes and the environmental fate of released (agro)chemicals should be conducted to improve existing models and develop new models describing the volatilization of pesticides from soils and crops.

5. CONCLUSIONS

The following findings were obtained from the measurement of volatilization rates and comparison with model approaches:

- The different volatilization rates of fluoranthene and diflufenican showed a clear correlation with their physicochemical properties. This is in agreement with earlier findings in the literature.
- Application of the *Behavior Assessment Model* led to the identification of soil moisture as the most critical parameter. Furthermore the model was not able to reflect non-equilibrium conditions during the initial stages.
- In spite of the varying quality of calculations using both screening-level approaches referring to the chosen compounds, general tendencies exhibited conformity.
- The observed discrepancies between measured and calculated volatilization rates illustrate the need for improving current descriptions.

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